An optical limiter based on ferrofluids

Swapna S. Nair,[1] Jinto Thomas,[2,3] C. S. Suchand Sandeep,[2] M. R. Anantharaman,[1] and Reji Philip[2,a)]
[1]*Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India*
[2]*Light and Matter Physics Group, Raman Research Institute, Bangalore 560 080, India*
[3]*Institute for Plasma Research, Gandhinagar 348 428, India*

(Received 19 March 2008; accepted 7 April 2008; published online 1 May 2008)

We report an optical limiter based on ferrofluids which has a very high shelf life and remarkable thermal stability, which are important requirements for sustainable use with intense lasers. The colloidal suspensions contain nanosized particles of approximately 80 Å diameter, with a number density of the order of $10^{22}/m^3$. The nonlinear optical transmission of the samples is studied using nanosecond and femtosecond laser pulses. Excited state absorption phenomena contribute to enhanced limiting in the nanosecond excitation regime. An advantageous feature of ferrofluids in terms of device applications is that their optical properties are controllable by an external magnetic field. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919052]

Ferrofluids are stable colloidal suspensions of nanomagnetic materials, typically magnetite or cobalt, suspended in a suitable base fluid.[1] Magnetite ferrofluids, which are the oldest ferrofluids, are widely used due to their very high saturation magnetization, good thermal stability, and stability against agglomeration.[2] These smart fluids have been extensively used in many engineering applications such as in loud speaker coils and pressure sensors. The magnetic field induced structural anisotropy of ferrofluids leads to many special magneto-optical properties such as field induced optical birefringence, linear and circular dichroism, Faraday rotation, and ellipticity. They also show many field independent properties such as zero field birefringence.[3–7]

An ideal optical limiter should be transparent to low energy laser pulses and opaque at high energies, so that it can protect human eyes and optical sensors from intense laser radiation. Several organic and inorganic compounds[8] and metal and semiconductor nanoparticles[9–11] are found to exhibit good optical limiting properties. However, optical limiting studies have not been reported for ferrofluids so far. In fact, it is the physical and chemical stability of ferrofluids, which is an important attribute for an optical limiter, which prompted us to investigate their optical limiting properties.

Precursor fine particles of magnetite were synthesized by cold coprecipitation from the aqueous solutions of $FeSO_4$ $7H_2O$ and $FeCl_3$ taken in the molar ratio 1*M* and 2*M*, respectively, for preparing sample FF1 (FerroFluid1). For synthesizing FF2 (FerroFluid2), 0.2*M* $NiSO_4$ $7H_2O$, 0.8*M* $FeSO_4$ $7H_2O$, and $FeCl_3$ were taken. *In situ* coating with the surfactant oleic acid was effected within the aqueous medium itself. Finally, the wet slurry was washed with acetone to remove all traces of water and was dispersed in the base fluid kerosene with the help of a sonicator. The colloidal suspensions contain nanosized particles with a number density of the order of $10^{22}/m^3$.

X-ray diffraction (XRD) patterns of the dried precursor samples and that of the ferrofluid were recorded in an x-ray diffractometer (Rigaku D max-C) using Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å), and planes were identified using the JCPDS (Joint Committee on Powder Diffraction Standards) tables.[12] The XRD spectrum of the magnetite ferrofluids is depicted in Fig. 1. The average particle sizes of these powder samples were estimated from the Debye Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \tag{1}$$

where λ is wavelength of x ray used, β is the full width at half maximum (FWHM) of the XRD peak with the highest intensity, and D is the particle diameter. From the measured line broadening, the particle size is calculated to be around 80 Å and the planes are identified. The lattice parameter "a" evaluated assuming cubic symmetry is found to be 8.314 Å.

The optical absorption spectrum of the magnetite-based ferrofluids is shown in Fig. 2(a). The band gap (assuming direct band gap) E_g is calculated from the expression for the absorption coefficient near the band edge, given by

$$\alpha = \frac{A(h\nu - E_g)^{1/3}}{h\nu}, \tag{2}$$

where A is a constant. When $\alpha h\nu = 0$, $E_g = h\nu$ and therefore, using an extrapolation, as shown in Fig. 2(b), E_g is determined to be 3.01 eV (412.2 nm).

Optical limiting measurements were carried out using laser pulses of 7 ns as well as 100 fs durations (FWHM). The laser pulses were plane polarized and had a Gaussian spatial profile. Samples were taken in a 1 mm cuvette. The intensity dependent light transmission through the sample

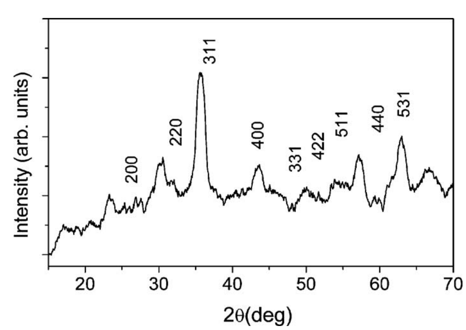

FIG. 1. XRD spectrum of magnetite ferrofluids.

a)Electronic mail: reji@rri.res.in.

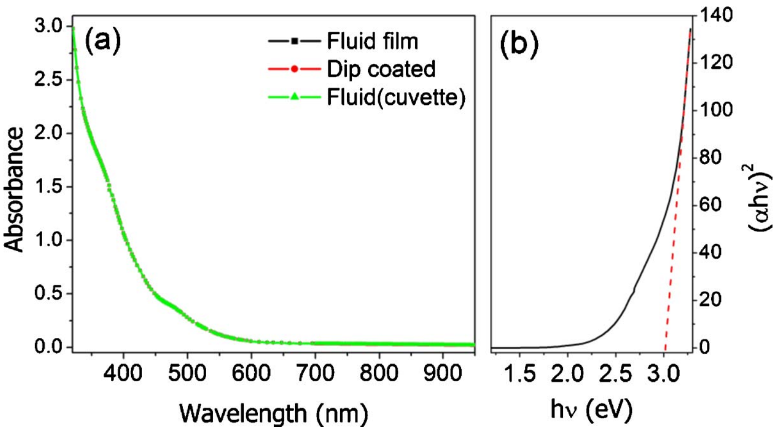

FIG. 2. (Color online) (a) Linear absorption spectra of the ferrofluid sample FF1 in different forms. (b) Optical band gap determination of Fe_3O_4 ferrofluids using Tauc plots.

was measured using an automated open aperture z-scan[13] setup. In the z-scan technique, the laser beam is focused using a lens, and the sample is moved along the beam axis (z axis) from one side of the focus to the other, through the focal point. In this scheme, each z position corresponds to an input fluence of $4\sqrt{\ln 2}E_{\text{in}}/\pi^{3/2}\omega(z)^2$, where E_{in} is the input laser pulse energy. $\omega(z)$ is the beam radius given by $\omega(0)/[1+(z/z_0)^2]^{1/2}$ where $\omega(0)$ is the beam radius at the focus, and $z_0=\pi\omega_0^2/\lambda$ is the Rayleigh range. Thus, at each position z the sample sees a different laser fluence, and the fluence will be a maximum at the focal point. The normalized transmittance of the samples (transmission normalized to the linear transmission of the sample) are plotted as a function of the incident laser fluence in, Figs. 3 and 4. For both wavelengths used, the samples show a minimum transmission around the beam focus, showing that the nonlinearity is of the optical limiting type.

We have studied the samples at two different concentrations, in addition to the pure base fluid. Samples having linear transmissions of 0.50 and 0.70 at the respective wavelengths are employed for all measurements. When excited with nanosecond pulses at 532 nm, the base fluid kerosene shows a weak limiting while the ferrofluid suspensions show a stronger limiting behavior (Fig. 3). The nonlinearity fits to a three-photon absorption process and the transmission is given by the equation[14]

$$T=\frac{(1-R)^2\exp(-\alpha L)}{\sqrt{\pi}p_0}\int_{-\infty}^{+\infty}\ln[\sqrt{1+p_0{}^2\exp(-2t^2)}+p_0\exp(-t^2)]dt, \quad (3)$$

where $p_0=[2\gamma(1-R)^2I_0^2L_{\text{eff}}]^{1/2}$. Here, R is the Fresnel reflection coefficient at the sample-air interface, α is the absorption coefficient, L is the sample length, and I_0 is the incident intensity. L_{eff} is given by $[1-\exp(-2\alpha L)]/2\alpha$. The three-photon absorption coefficients (γ) obtained are in the order of 10^{-22} m^3/W^2. This nonlinearity arises from two-photon absorption followed by excited state absorption, which can be considered as an "effective" three-photon absorption process. For instance, such an effective $\chi^{(5)}$ nonlinearity of the $\chi^{(3)}:\chi^{(1)}$ type has been observed in semiconductors[15] and metal nanoparticles[11,16] where the excited state absorption is brought about by free charge carriers.

Figure 4 shows the nonlinear transmission curves obtained with 100 fs pulses, at the excitation wavelength of 800 nm. Limiting in the base fluid is only slightly less than that exhibited by the samples. All the three curves fit to a three-photon absorption process. Considering the very short timescale and the high intensities involved, genuine three-photon absorption should be responsible for the limiting in this case. Addition of the ferrofluids only marginally improves the inherent optical limiting property of kerosene in the femtosecond regime. The corresponding three-photon ab-

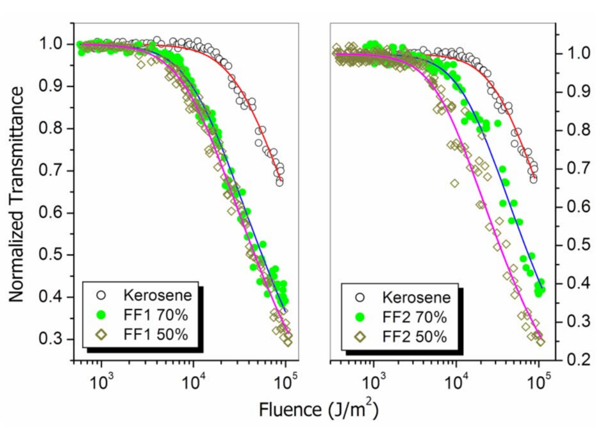

FIG. 3. (Color online) Fluence dependent transmission of the base fluid and the samples for 532 nm, 7 ns laser pulse excitation. Sample linear transmissions are shown in the inset. Circles denote experimental data and the solid curves are numerical fits.

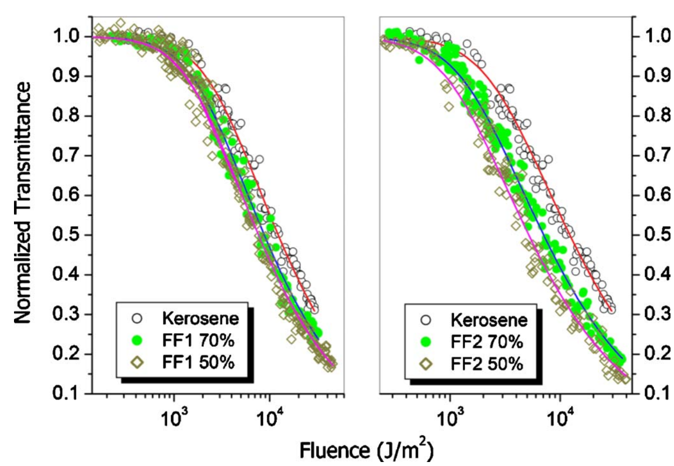

FIG. 4. (Color online) Fluence dependent transmission of the base fluid and the samples for 800 nm, 100 fs laser pulse excitation. Sample linear transmissions are given in the inset. Circles denote experimental data and the solid curves are numerical fits.

sorption coefficients are in the order of 10^{-30} m^3/W^2, which is much lower than the value obtained for nanosecond excitation at 532 nm. Resonance enhancement of the nonlinearity and enhanced excited state absorption are the factors contributing to the higher value in the latter case.

In conclusion, we have experimentally shown that ferrofluids are potential candidates for optical power limiting. The good thermal stability, resistance against agglomeration, and long shelf life make them attractive for this application. A specific advantage of ferrofluids is that the optical properties in these materials are tunable by an applied magnetic field. For instance, upon the application of the magnetic field, the linear transmission along the *x*-*y* plane could be changed by 235%, because of the formation of periodic chainlike structures.[17] In a typical device application, such magnetocontrollability can turn out to be very useful.

[1]R. E. Rosenweig, *Ferro Hydrodynamics* (Cambridge University Press, New York, 1985).
[2]R. K. Bhat, Ind. J. Eng. Mater. Sci. **5**, 477 (1998).
[3]J. Smit and H. P. G. Wijn, *Ferrites* (Philips Technical Library, Eindhoven, 1959).
[4]J. Deperiot, G. J. Da Silva, and C. R. Alves, Braz. J. Phys. **31**, 390 (2001).
[5]E. Hasmonay and J. Depeyrot, J. Appl. Phys. **88**, 6628 (2000).
[6]G. M. Sutharia and R. V Upadhyaya, Ind. J. Eng. Mater. Sci. **5**, 347 (1998).
[7]K. T. Wu, P. C. Kuo, Y. D. Yao, and E. H. Tsai, IEEE Trans. Magn. **37**, 2651 (2001).
[8]L. W. Tutt and T. F. Boggess, Prog. Quantum Electron. **17**, 299 (1993).
[9]R. Philip, G. Ravindra Kumar, N. Sandhyarani, and T. Pradeep, Phys. Rev. B **62**, 13160 (2000).
[10]S. Link, C. Burda, Z. L. Wang, and M. A. El-Sayed, J. Chem. Phys. **111**, 1255 (1999).
[11]P. V. Kamat, M. Flumiani, and G. V. Hartland, J. Phys. Chem. B **102**, 3123 (1998).
[12]JCPDS-ICDD C Card No. 10-319 (1990).
[13]M. Sheik Bahae, A. A. Said, and E. W. Van Stryland, Opt. Lett. **14**, 955 (1989).
[14]R. L. Sutherland, *Handbook of Nonlinear Optics* (Dekker, NY, 1996).
[15]A. A. Said, C. Wamsley, D. J. Hagan, E. W. Van Stryland, B. A. Reinhardt, P. Roderer, and A. G. Dillard, Chem. Phys. Lett. **228**, 646 (1994).
[16]J. Thomas, M. Anija, J. Cyriac, T. Pradeep, and R. Philip, Chem. Phys. Lett. **403**, 308 (2005).
[17]Swapna S. Nair, S. Rajesh, V. S. Abraham, M. R. Anantharaman, and V. P. N. Nampoori, J. Magn. Magn. Mater. **304**, 28 (2006).